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THE ROLE OF REACTIVE FUNCTIONAL GROUPS IN ADHESIVE

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BONDING AT THE ARAMID-EPOXY INTERFACE (U) MIDWEST  
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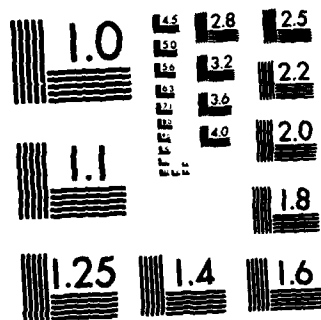
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11. The Role of Reactive Functional Groups in Adhesive Bonding at the Aramid-Epoxy Interface (Unclassified).

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19. → and the epoxy molecule showed that covalent bonding did not occur, thus explaining the unexpected lack of improvement in adhesive performance. ↗

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FINAL REPORT

THE ROLE OF REACTIVE FUNCTIONAL GROUPS  
IN ADHESIVE BONDING AT THE ARAMID-EPOXY INTERFACE

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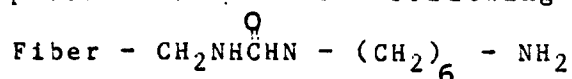
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## INTRODUCTION

In polymeric composites, the presence of reactive functional groups on the fiber surface is expected to greatly enhance the mechanical strength of the fiber-matrix interface through a covalent bonding mechanism. However, whether the functional groups actually form covalent bonds with a matrix has not been demonstrated directly. One reason for this is that it is difficult to evaluate the contribution of covalent bonding to interfacial adhesion in the presence of the varying contributions of surface energetics and surface topography. In the work described in this report we sought to promote covalent bonding at the interface by attaching flexible reactive pendent groups to the surface of aramid fiber. At the same time, we attempted to keep the fiber surface topography and the fiber surface energetics constant. This approach had two goals: a) to determine the contribution of reactive pendent groups to covalent bonding at the interface, and b) to assess the role of covalent bonding in adhesion at the interface.

## RESULTS AND DISCUSSION

This section briefly describes the procedures and their results. Details are given elsewhere (1). The first step was to activate the inert aramid fiber surface by plasma treatment with monomethylamine gas. This has been reported to attach the amino methyl group to the aromatic ring of the fiber polymers chain (2,3). Groups attached by the plasma treatment were extended by chemical reaction with 1,6-diisocyanatohexane (NCO). After removal of unreacted NCO and conversion of terminal isocyanate groups to primary amine, the pendent group were presumed to have the following structure:



This structure contains terminal amine for reaction with the epoxy molecule of subsequently applied matrix. It also contains a six-carbon aliphatic segment to enhance the accessibility to the terminal amine (4,5). Finally, its urea linkage can be hydrolytically cleaved to release 1,6-diaminohexane for quantitative analysis in solution.

Scanning electron microscopy showed that the plasma treatment left the original smooth fiber surface intact and did not etch it. SEM also showed that no irregular deposits were left on the surface after the NCO addition.

Wettability analysis by the Wilhelmy method (6) showed that only minor changes in surface energetics occurred as a result of the attachment of pendent groups. The changes were interpreted as introduction of microscopic regions of reduced polarity having their origin in the oleophilic six-carbon segments of the pendent groups. A change in surface polarity of the modest magnitude detected here has been found to have no effect on fiber-matrix adhesion in similar situations (7,8).



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Combined results from infrared spectroscopy (attenuated total reflectance) and x-ray photoelectron spectroscopy (XPS) studies showed that aramid fiber without any treatment (control) possessed a partially oxidized surface. Part of the oxygen was in the form of hydroxyl groups. XPS showed that further oxidation was the most noticeable change in the fiber surface as a result of the monomethylamine plasma treatment. This result, often observed in plasma treatment, may be explained by the reaction of air with residual free radicals on the fiber surface when the fiber was removed from the plasma reactor. For the NCO-treated fiber, IR showed the presence of aliphatic  $\text{-CH}_2\text{-}$  and XPS showed an increase in C and N atoms at the surface, all consistent with presence of the pendent group.

For quantitative analysis, the pendent groups attached to the treated fiber surface were cleaved at the urea linkage by high pressure steam to release 1,6-diaminohexane into the cleavage medium. The effectiveness of the steam hydrolysis procedure in cleaving the pendent group without cleaving the fiber polymer chains was checked on model compounds. One compound modelled the urea linkage of the pendent group and the other compound modelled the amide linkage of the fiber polymer chain. The cleavage conditions developed succeeded in hydrolyzing 95% of the urea model compound to primary amine while hydrolyzing less than 7% of the amide model compound. Survivability of primary amine under the cleavage conditions was also checked and found to be  $> 80\%$ .

The cleavage solution was subjected to a fluorescence assay specific for primary amine (9). The fluorescence assay results showed that treated fiber contained pendent groups at the level of 1.5 - 4.5 groups per  $100\text{\AA}^2$  of fiber surface. This is well above the background level of  $0.78 \pm 0.31$  groups per  $100\text{\AA}^2$  obtained on control fiber. The level of attachment is in good agreement with the theoretical maximum of 4 groups per  $100\text{\AA}^2$ , computed from fiber polymer chemistry and crystal structure (10).

Repeated cycles of NCO addition and cleavage on the same fiber specimens showed that pendent groups could be cleaved and regenerated indefinitely. Another important finding was that the duration of the plasma treatment prior to NCO addition had no effect on the number of pendent groups attached by NCO. This, plus the fact that both control and plasma-treated fiber surface were oxidized and contained  $\text{-OH}$  groups led us to suspect that much of the pendent group formation occurred by addition of NCO to the  $\text{-OH}$  group forming a urethane linkage (also cleavable like urea). To test this, we treated control fiber with NCO and found that the same amount of pendent groups were formed as with the plasma-treated fiber. Thus it appears that the plasma treatment is not a prerequisite for activating the aramid surface. It is apparently already activated with a high level of  $\text{-OH}$  groups which serve as sites for pendent group attachment.



The adhesive bond strength at the fiber-matrix interface of treated and untreated fiber was evaluated directly by a single filament pull-out test (11, 12). The matrix resin was a common epoxy cured with analiphatic amine at 120°C for 3 hr. Table 1 shows two major findings.

Table 1. Interfacial Bond Strengths (Ave. + Std. Dev.) for Control and Fully-Treated Aramid Fibers in Epoxy Matrix

<u>Fiber Treatment</u>	<u>Interfacial Bond Strength, psi</u>	<u>No. Specimens,</u> <u>N</u>
None (control)	4940 + 820	26
2-min plasma plus NCO	4960 + 1040	23
5-min plasma plus NCO	4650 + 1140	45
15-min plasma plus NCO	4520 + 1160	32

First, the adhesive bond strength at the interface was not improved by the presence of flexible reactive pendent group. Second, the adhesive bond strength was insensitive to the difference in plasma treatment times prior to the NCO addition. The latter finding has already been explained by the fact that all treated fiber contained the same number of pendent groups, no matter what the plasma treatment time. The former finding, however, required further explanation.

To explain this, a specific test for covalent bonding between the pendent groups terminal amine and the epoxide ring of an epoxy molecule was conducted. From a group of ten identical fully treated (5-min plasma plus NCO) fiber specimens, five were reserved and five exposed to reactive liquid epoxy. The epoxy, a monofunctional model of those used in matrix resin, was used without curing agent to eliminate competing reactions. Chemical reaction between the epoxide ring of the epoxy molecule and the terminal primary amine of the pendent group would transform the primary amine to secondary amine, a species which cannot be detected by our fluorescence assay method. Therefore a reduction in fluorescence assay values would signify that reaction had occurred. Cleavage and fluorescence assay were performed on the reserved specimens and on the epoxy-exposed specimens. The results were identical :  $2.61 \pm 0.41$  groups/100 Å<sup>2</sup> on the unexposed fiber and  $2.56 \pm 0.42$  groups/100 Å<sup>2</sup> on the epoxy-exposed fiber. This indicated that there was no chemical reaction between the pendent groups and the epoxy. This unexpected result is one of the most important findings of this work.

### CONCLUSIONS

The key findings of this work are summarized briefly below.

1. Pendent groups, each containing a flexible six-carbon aliphatic segment and a terminal primary amine, were covalently attached to the aramid fiber surface.
2. The groups were chemically attached through the hydroxyl groups already present on the untreated fiber surface or through the

aminomethyl groups placed on the surface by plasma activation or through both.

3. Quantitative analysis of pendent groups showed surface attachment levels of 1.5 - 4.5 groups/100 Å<sup>2</sup> agreeing with the theoretical maximum of 4 groups/100 Å<sup>2</sup>.
4. Mechanical tests of the adhesive strength between fiber with pendent groups and epoxy matrix showed no improvement over the adhesive strength between control fiber and epoxy matrix.
5. Specific chemical tests for the reaction of pendent groups with epoxy molecules showed that no reaction took place.

The general conclusion to be drawn from these findings is that, contrary to common assumption, reactive functional groups on a fiber surface do not necessarily form covalent bonds with a reactive matrix. In the case reported here, that fact that there was no chemical reaction between the pendent groups and the epoxy molecule precluded the improvement of fiber-matrix adhesion by a covalent bonding mechanism. It is, of course, still reasonable to assume that if covalent bonding between the fiber and matrix could be achieved, adhesive bonding would be improved.

The question that remains from this work is why the particular pendent groups, designed to be accessible and reactive, did not react with the epoxy. A preferred conformation (e.g. to minimize surface energy) may have rendered the terminal amines inaccessible. This question is the subject of continuing research.

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